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# Contaminants from the Reaction of Aerozine 50 with MIL-L-7808D1

Prepared by H. H. TAKIMOTO and G. C. DENAULT
Aerodynamics and Propulsion Research Laboratory

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Laboratory Operations
AEROSPACE CORPORATION

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AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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## FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04701-68-C-0200 and documents research carried out from July through August 1968. This report was forwarded to Lt. J. F. Turk, SMTTP, for review and approval on 8 November 1968.

Approved

G. W. King

G. W. King, Vice President and
Operations General Manager
Laboratory Operations

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Approved

John F. Turk

John F. Turk, 2nd Lt, USAF
Project Officer

## ABSTRACT

The solid contaminants found deposited in the cavity between the fuel pump and the gear box of the Titan boosters have been analyzed and identified to be composed primarily of azelaic acid dihydrazide. This product was shown to have resulted from the interaction of Aerozine 50 and the hydraulic fluid, MIL-L-7808D1 oil, from the gear box. Its structure was conclusively established by an independent synthesis of an authentic sample.

CONTENTS



FIGURE

# I. INTRODUCTION

Solid contaminants found on the propellant fuel side of the Titan booster (Stages 1 and 2) assembly at Aerojet-General Corporation, Sacramento, have been received for chemical analyses. These solids were deposited in the cavity between the fuel pump and the gear box and were generally associated with the leakage of the hydraulic fluid in the gear box. Although the presence of these materials had been observed periodically for a number of years during cleaning and dismantling operations, the analyses of these contaminants had not been carried out since no serious performance problem attributable to these solids had been reported. This report describes the investigation of the contaminants and the identification of their major product as the dihydrazide of azelaic acid resulting from the reaction of the hydraulic fluid with Aerozine 50.

## II. RESULTS AND DISCUSSION

Since the contaminants were generally found in the vicinity of the gear box containing the hydraulic fluid, the possibility of the deposit resulting from the interaction of the fuel with the oil that had leaked into the propellant system was investigated. Bray Oil Co. Conojet 880 (MIL-L-7808D1 oil) was analyzed and estimated by Aerojet-General Corporation to be composed of the following:

| | |
|---|---|
| 47% | Diiso-octyl azelate |
| 47% | Dipropyleneglycol dipelargonate |
| 4.5% | Tricresyl phosphate, plasticizer |
| 0.5% | Phenathiazine, oxidation inhibitor |
| X% | Azelaic acid (impurity) |

Based on the above composition, the carbon, hydrogen, and nitrogen content of the oil can be calculated. As a check on this composition, elemental analyses were carried out. The comparison of the calculated values together with the experimentally determined percentages are shown below:

Analyses of MIL-L-7808D1 Oil

| Element | Found (%) | Calculated (%) |
|---|---|---|
| Carbon | 70.92 | 70.46 |
| Hydrogen | 10.93 | 11.05 |
| Nitrogen | 0.11 | 0.04 |

The results are consistent with the estimated composition of the hydraulic fluid.

The contaminants as received in the laboratory were greenish-gray, waxy solids having a strong amine odor. These materials only partially dissolved in common organic solvents in the cold such as ethanol, acetone, chloroform, and ethyl acetate. They did not dissolve in Freon MF solvent.

Recrystallizations of the crude contaminants from hot ethanol yielded two products. Both were white crystalline solids having similar infrared spectra. After repeated purification, one product melted at 186 to 186.5°C (Compound I), and the second melted at 75 to 78°C (Compound II). The former compound constituted the major portion of the contaminants. Elemental analyses of Compound I gave the values consistent with the empirical formula, $C_9H_{20}O_2N_4$. The values are listed below.

Analyses of the Major Contaminant, Compound I

| Element | Found (%) | Calculated for $C_9H_{20}O_2N_4$ (%) |
|---|---|---|
| Carbon | 50.21 | 49.98 |
| Hydrogen | 9.28 | 9.32 |
| Nitrogen | 25.63 | 25.91 |
| Oxygen | 14.88[a] | 14.79 |

[a]Obtained by difference

An insufficient quantity of Compound II, the minor constituent, was obtained, preventing further analyses.

In order to verify that the above contaminants resulted from the reaction of the fuel with the hydraulic fluid, a few drops of the oil were added to Aerozine 50. After the mixture stood at room temperature for several hours, a white solid separated out. This solid was collected by filtration and found to melt at 168 to 175°C. Upon recrystallization from ethanol, the product melted at 185 to 186°C. A mixed melting point of the product with Compound I exhibited no depression, indicating that they were identical compounds. An infrared spectrum taken on this material exhibited absorption bands essentially identical to Compound I (Fig. 1). These results conclusively prove that the origin of the solid deposit in the fuel side resulted from the reaction of the oil, which had leaked out, with Aerozine 50.

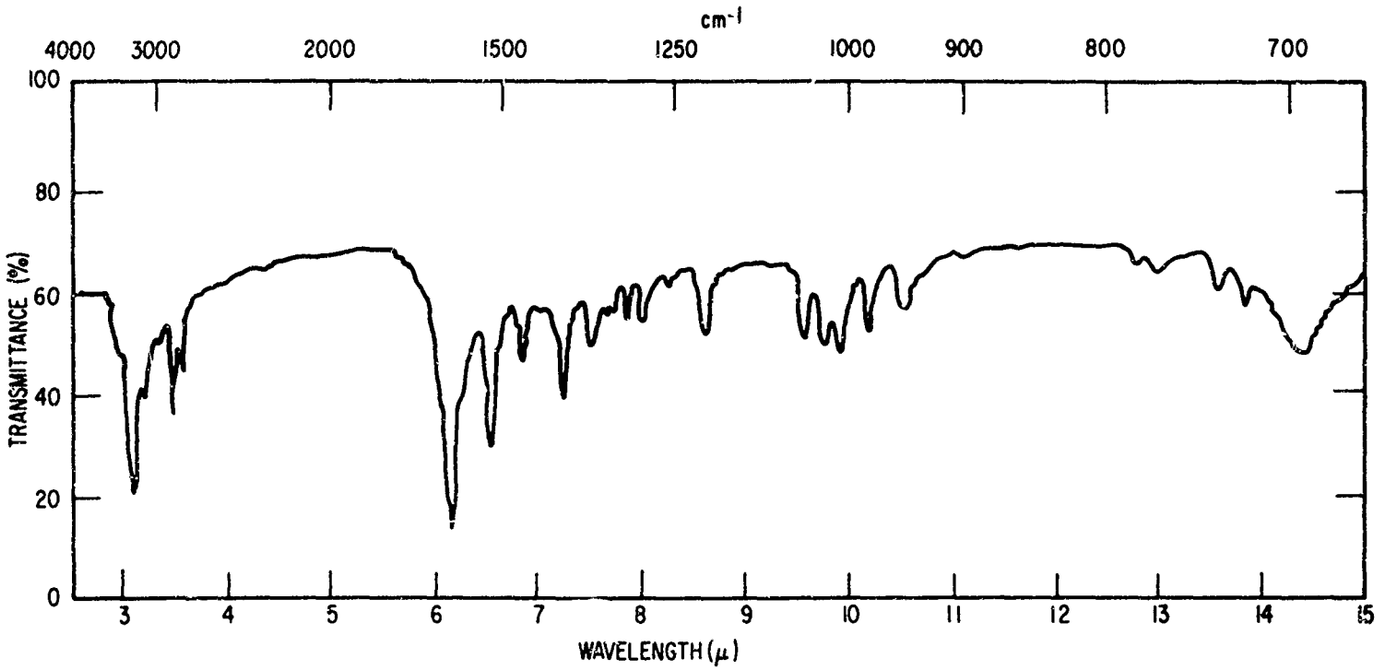


Figure 1. Infrared Spectrum of Azelaic Acid Dihydrazide.

Although the origin of the fuel contamination was established, the chemical nature of the solid still remained in question. Since the major constituents of MIL-L-7808D1 are esters, namely diiso-octyl azelate and dipropyleneglycol dipelargonate, it seems reasonable to expect the contaminant to be the reaction product of the propellant with one or both of these esters. The ammonolysis reaction between esters and ammonia to form amides is well documented. Similarly, esters and hydrazine undergo hydrazinolysis when the alkoxy group is replaced with a hydrazine group. Such reaction of the major constituents of MIL-L-7808D1 with the fuel would yield the di- and the mono-hydrazide of azelaic and pelargonic acids, respectively. The former compound has an empirical formula, $C_9H_{20}O_2N_4$, which is identical to Compound I obtained from the purification of the contaminant.

In order to test whether Compound I is indeed azelaic acid dihydrazide, an authentic sample of this product was prepared independently in the laboratory. The treatment of azelaic acid with thionyl chloride yielded the corresponding acid chloride, its conversion with methanol gave the diester, and finally, the hydrazinolysis reaction was carried out to form azelaic acid dihydrazide. The synthetic scheme is outlined below:

$$HO_2C\text{-}(CH_2)_7\text{-}CO_2H \xrightarrow{SOCl_2} Cl\text{-}CO\text{-}(CH_2)_7\text{-}CO\text{-}Cl \xrightarrow{ROH} RO_2C\text{-}(CH_2)_7\text{-}CO_2R \xrightarrow{N_2H_4} N_2H_3\text{-}CO\text{-}(CH_2)_7\text{-}CON_2H_3$$

azelaic acid dihydrazide

Azelaic acid dihydrazide, thus synthesized, was shown to be identical to Compound I by (1) its melting point (reported value, 187°C[1]), (2) no depression in the mixed melting point of the two products, and (3) infrared spectra.

[1] R. F. Paschke and D. H. Wheeler, J. Am. Oil Chemists Soc. 26, 637-8 (1949).

The problem of solid deposition in the cavity between the gear box and the fuel pump will continue as long as the fuel can come in contact with MIL-L-7808D1 oil. Organic esters present in the hydraulic fluid will readily undergo hydrazinolysis reaction, generally leading to solid products. By minimizing the leakage of oil, the buildup of the deposit can be decreased. Alternatively, cleaning the cavity with a solvent, which will dissolve the major portion of the contaminants, is more desirable than complete dismantling of the parts. Warm alcohol or hot water will dissolve the bulk of this contaminant. Another possible solution is changing the constituents of the oil by replacing the esters with fluids that are compatible with the fuel.

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